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THE CANMET FERRIC CHLORIDE LEACH PROCESS

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THE CANMET FERRIC CHLORIDE LEACH PROCESS

by

D.H. BELL

ABSTRACT

A Ferric Chloride Leach process has been developed by CANMET to recover zinc, lead, silver and copper from bulk complex sulphide concentrates. Metal recoveries are high: zinc 99%, lead 99.5%, copper 98% and silver 96.5%. Sulphur appears as inert sulphide and elemental sulphur in the leach residue and can be recovered. Minor metals such as cadmium, bismuth, antimony and arsenic are recovered by cementation or precipitation. Spent liquors are rechlorinated with chlorine from the electrowinning of lead and zinc and recycled to leach. The process consists of a two stage leach, crystallization of lead chloride from the leach liquor, cementation of silver and copper on iron and separation of zinc chloride by solvent extraction. Zinc chloride solution is further purified by a novel solvent extraction step and by cementation of copper and other impurities on zinc dust. Zinc is electrowon as Special High Grade quality cathodes from the chloride electrolyte. Lead is electrowon from lead chloride by either aqueous or molten salt electrolysis. Impurity build-up is controlled by a bleed stream, which undergoes oxyhydrolysis for recovery of chloride and metal values. The CANMET FCL process eliminates SO_2 emission from sulphide ore treatment and reduces solid and liquid effluents to a minimum. The solid residue can be treated for gold recovery if warranted.

Keywords: Extractive Metallurgy, zinc, lead, silver, copper, ferric chloride, leaching, zinc solvent extraction, zinc electrowinning from chloride solution

PROCÉDÉ DE LESSIVAGE AU CHLORURE FERRIQUE DÉVELOPPÉ PAR CANMET

par

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RÉSUMÉ

Un procédé de lessivage au chlorure ferrique a été développé par CANMET en vue de récupérer le zinc, le plomb, l'argent et le cuivre d'une quantité importante de concentrés sulfurés complexes. La récupération des métaux a été élevée : 99 % de zinc, 99,5 % de plomb, 98 % de cuivre et 96,5 % d'argent. Le soufre, qui peut être récupéré, est présent sous forme de sulfure inerte et de soufre (élément) dans les résidus de lixiviation. Les métaux moins importants, comme le cadmium, le bismuth, l'antimoine et l'arsenic sont récupérés par cémentation ou précipitation. Les solutions épuisées sont rechlorées avec du chlore provenant de l'électro extraction du plomb et du zinc, et recyclées comme solution de lixivation. Le procédé comprend le lessivage à deux étages, la cristallisation du chlorure ferrique provenant de la solution de lixivation, la cémentation de l'argent et du cuivre par le fer et la séparation du chlorure de zinc par extraction au solvant. La solution de chlorure de zinc est à nouveau épurée par une étape d'extraction au solvant et par la cémentation du cuivre et autres impuretés par la poussière de zinc. Le zinc est extrait par électrolyse de l'électrolyte chloraté en tant que cathode spécial de haute qualité. Le plomb est extrait par électrolyse du chlorure de plomb soit avec des électrolytes aqueux ou composés de sels fondus. Les dépôts d'impuretés sont contrôlés au moyen d'un robinet purgeur qui est en suite oxyhydrolisé pour la récupération du chlorure et des valeurs des métaux. Le procédé de lessivage au chlorure ferrique développé par CANMET (FCL), élimine les émissions d'anhydride sulfureux (SO_2) lors du traitement d'un minerai sulfuré et réduit les effluents solides et liquides à un minimum. Il est possible de traiter le résidu solide en vue de récupérer l'or qu'il contient, le cas échéant.

Mots-clé : Métallurgie extractive, zinc, plomb, argent, cuivre, chlorure de fer, lessivage, extraction par solvant au zinc, électrolyse du zinc contenu dans une solution chlorurée

THE CANMET FERRIC CHLORIDE LEACH PROCESS

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THE CANMET FERRIC CHLORIDE LEACH PROCESS

1. Summary

CANMET has developed a Ferric Chloride Leach (FCL) Process for the hydrometallurgical treatment of bulk concentrates from complex zinc-lead-copper-silver sulphide ores. The process extracts 99% of the lead and zinc, and more than 95% of the copper and silver from the concentrate feed. Zinc is produced as a SHG cathode product by aqueous electrowinning; lead of corroding grade quality is produced by molten salt electrolysis of $PbCl_2$; copper and silver are produced as a high-grade cement product suitable as feed to a copper smelter and sulphur reports to the leach residue as elemental sulphur and unreacted sulphides (mostly pyrite).

The process involves two-stage leaching of the concentrate in ferric chloride, the separation of $PbCl_2$ by crystallization, the cementation of copper and silver on iron, followed by the separation of zinc chloride by solvent extraction. The flowsheet is shown in Figure 1. The ferric chloride lixiviant is regenerated by direct chlorination using the chlorine generated in the electrowinning of zinc and lead. Impurity buildup and iron balance are controlled by taking a bleed stream from the SX raffinate. The SX raffinate is treated for by-product cadmium recovery. The bleed stream in treated by oxyhydrolysis to recover and recycle HCl and contained metal values (zinc, lead, cadmium, etc.). An environmentally acceptable residue is disposed to tailings.

The capital cost of a 100,000 MTPY zinc plant, using the FCL process, has been estimated at $186 million (Can.). Operating costs, excluding amortization and depreciation, are estimated to be 55c/kg of zinc. By-product credits from the sale of lead, silver, copper, cadmium and possibly sulphur will substantially

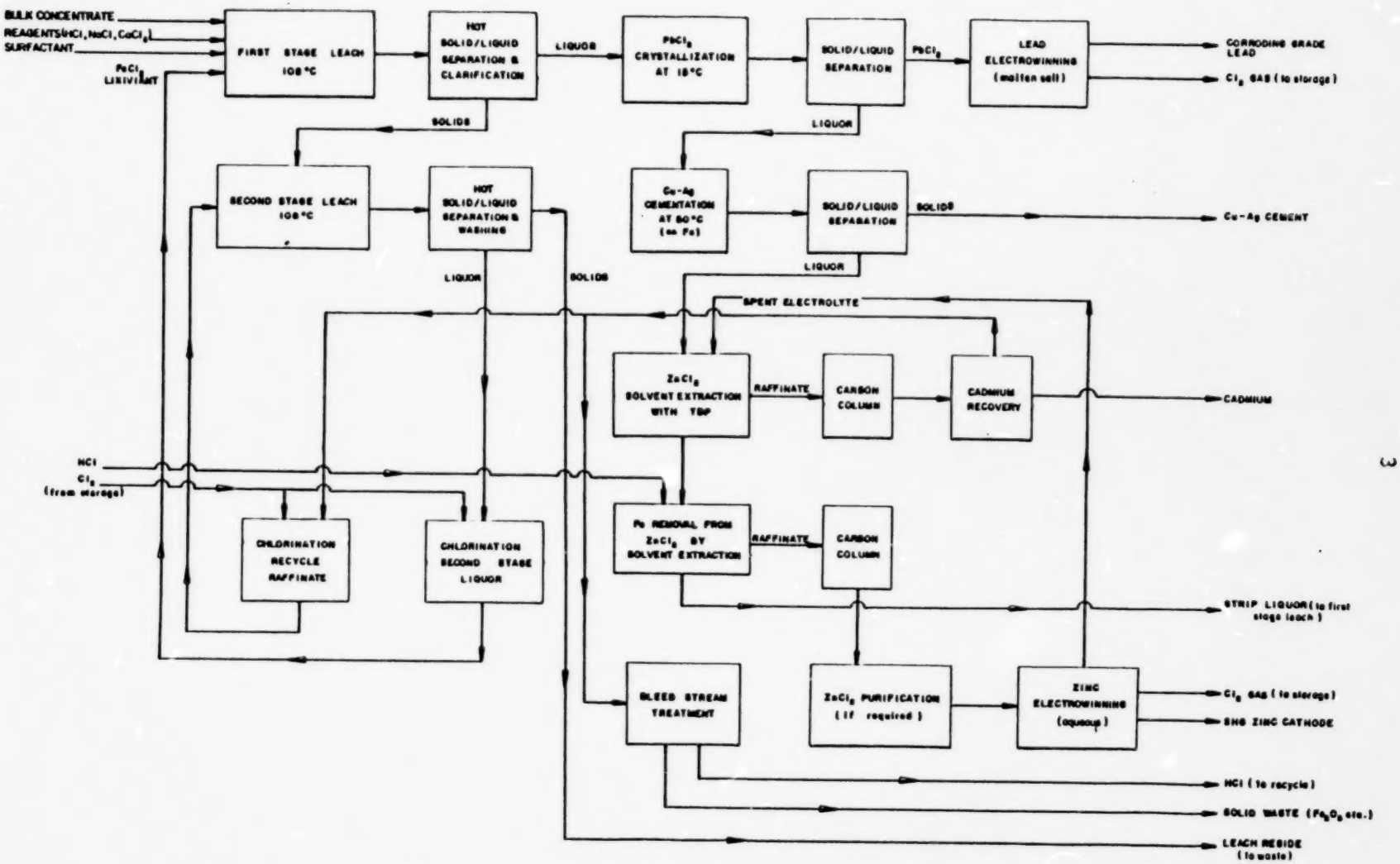

FIGURE 1

THE CANMET FERRIC CHLORIDE LEACH PROCESS

reduce this operating cost. Initial estimates indicate that the FCL process can provide significant economic benefits over conventional processes either as a grass roots plant or as an add-on to an existing facility. It will be particularly attractive for treating complex base metal sulphide ores, where high recoveries from the ore are dependent upon producing a low-grade, complex bulk concentrate. As part of an integrated mine/mill/smelter facility it will provide the mine/mill with the flexibility to produce high-grade selective concentrates if desired, while achieving high recoveries from the ore by producing a bulk concentrate for treatment in the FCL process.

The process has been shown to be technically viable and appears to be economically attractive. The process is ready to be taken to the pilot-plant stage of development. An industrial partner, in possession of an orebody that can benefit from this process, is being sought to participate in bringing this process to commercialization.

THE CANMET FERRIC CHLORIDE LEACH PROCESS

2. Introduction

Over the past decade, CANMET has been engaged in a research program to develop processes for the treatment of complex sulphide ores. Although directed at New Brunswick deposits, which are the largest reserves of lead, zinc and silver in Canada, the program has much broader applications as complex sulphide deposits of similar nature are found throughout the world.

Conventional processing of these ores typically involves selective flotation of zinc, copper and lead concentrates, and may include production of a bulk concentrate for processing in an Imperial Smelting Furnace. ISF technology imposes limitations on the grade and composition of the bulk concentrate, which results in significant loss of values to tailings in the mill. Although mineral dressing research improved metal value recoveries in the concentrator to about 75% (based on 1985 prices), further improvements require the production of bulk concentrates of lower grade and greater complexity than are currently produced. These concentrates would be unsuitable for conventional processing. There is a need, therefore, for new processing technology, which can accommodate the grade and complexity of these bulk concentrates.

The impact of acid rain on the environment is an increasing concern which will likely result in action by various government jurisdictions to reduce SO_2 emissions and apply more stringent environmental regulations in the future. Although sulphuric acid production has conventionally been used to reduce SO_2 emissions, marketing contraints on the acid make alternative solutions desirable.

CANMET identified chloride processing, from among a number of options, as the approach with the greatest potential for achieving the recovery and environmental objectives. After considerable research, the ferric chloride leach process (FCL) was selected as the most promising. The CANMET FCL process has been designed and developed to resolve these constraints which are associated with the processing of complex base metal sulphide ores.

3. The Ferric Chloride Leach (FCL) Process: General Description

The FCL process (see Figure 1) consists essentially of a 2-stage ferric chloride leach of the bulk concentrate feed, in which the first stage produces a fully reduced leach liquor. Overall extractions in the leach are 99% for the lead, 99% for the zinc, 97% for the copper and 96% for the silver. After solid-liquid separation and solution clarification, the solution is cooled to 15°C to precipitate lead chloride crystals of 99 +% purity. The lead chloride is filtered, washed and dried. Lead metal is produced by fused salt electrolysis of the lead chloride. The chlorine produced in electrolysis is used to regenerate the ferric chloride lixiviant for the leach stages. Copper and silver are removed to <1 ppm by cementation on iron granules.

The filtrate from the copper-silver cementation step typically contains 52 g/L zinc. Solvent extraction using tributyl-phosphate in Solvesso is used to extract zinc chloride from solution. The loaded organic is stripped with spent electrolyte from zinc electrowinning. Cadmium is recovered from the raffinate. A bleed stream is taken after cadmium recovery to control the buildup of iron and other impurities in the circuit. The bleed stream is treated for chloride recovery, and an environmentally acceptable solid residue is produced. The remainder of the raffinate is chlorinated and recycled to the leaching stage.

Traces of iron (FeIII) in the zinc chloride strip liquor are removed in a second solvent extraction circuit which produces an iron-free zinc chloride raffinate. The raffinate is passed through an activated carbon column to remove traces of organic reagent. If required, traces of copper, lead and cadmium can be removed by cementation on zinc dust, producing a pure zinc chloride solution for zinc electrowinning. The chlorine produced in zinc electrowinning is used to regenerate the ferric chloride lixiviant for the leaching stages. The iron-removal organic is stripped periodically with strong HCl and the strip liquor is recycled to the leach circuit.

4. The FCL Process - Detailed Description

4.1 Two-stage Leach

The bulk cencentrate feed to the FCL process typically contains about 28-30% zinc, 8-10% lead, <1% copper, about 250-300 ppm silver, 17-19% iron, about 33% sulphur and minor amounts of cadmium, bismuth, antimony and arsenic. The bulk concentrate feed is leached in two stages. The first stage lixiviant is the chlorinated ferric chloride liquor from the second stage leach. The solid residue from the first stage leach is subsequently leached in the second stage, with chlorinated recycle raffinate from zinc chloride solvent extraction. The second stage solids residue is washed, and sent to waste. With two-stage leaching the metal extractions achieved are:

zinc - >99%
lead - >99%
copper - 97.4%
silver - 95.8%

The leach conditions required for optimum metal extraction are shown in Table 1.

Table 4-1 - Optimum Leach Conditions

Condition		Stage 1	Stage 2
Solid: liquid ratio		162 g concentate/ litre lixiviant	99 g residue/litre lixiviant
Temperature		107-108°C	107-108°C
Composition -	$FeCl_3$	0.90 M (50 g/L)	0.90 M (50 g/L)
	HCl	0.11 M	0.11 M
	NaCl	3.0 M	3.0 M
	$CaCl_2$	50 kg/M.T. of concentrate	--
Retention time		3.0 h	4.5 h
Surfactant		0.25 kg/t of concentrate	
Wash water			2.5 x cake moisture

The first stage leach produces a leach liquor containing a maximum of 1 g/L of ferric iron. This specification minimizes the co-extraction of iron with zinc during solvent extraction and also minimizes iron consumption during copper-silver cementation. A ferric iron concentration of 0.90 M in the lixiviant limits the oxidation of sulphide sulphur to sulphate to about 3%. Calcium chloride is added to the leach to control the dissolved sulphate concentration by the precipitation of gypsum.

4.2 Leach Liquor Treatment

Clarified leach liquor is cooled to 15°C to crystallize $PbCl_2$. The quality of lead bullion produced in electrowinning is a direct function of $PbCl_2$ purity. Impurities which interfere with

bullion quality are SO_4, Fe, Cu, Bi, Sb and Ag. Test results indicate that impurity levels of <500 ppm SO_4 and <100 ppm Fe can be achieved when rapid cooling is used to minimize $CaSO_4$ precipitation, however, recrystallization may be required to produce corroding grade lead. The use of vacuum crystallizers has yet to be investigated, but it is felt that they will provide the best method of quality control.

Copper and silver are removed from the liquor by cementation on iron at 50°C. Iron consumption of 2.5 g/L yields a solution containing <1 mg/L of copper and silver, and a cement product containing 45% Cu, 1.2% Ag, 1.7% As, 1.7% Sb, 0.5% Pb and 34% Fe. The cement product is suitable as feed to a copper smelter. Upgrading of the cement product is possible where required to increase saleability.

4.3 Lead Electrowinning

A study was done for CANMET by the SNC Group to evaluate and compare the aqueous and molten salt technologies for lead electrowinning. The study reported that the technical feasibility of lead production from fused salt electrolysis of lead chloride crystals had been proven in pilot plant scale operations and concluded that the molten salt technologies developed by USBM or Alcoa should be adopted, as they were the most advanced; SNC preferred the USBM process. The estimated capital and operating costs indicated that the USBM process would be economically preferred, based on pilot-plant data.

4.4 Zinc Chloride Solvent Extraction

Zinc chloride is extracted from the leach liquor by solvent extraction with tributyl-phosphate (TBP) in Solvesso. The loaded organic is stripped with spent electrolyte from the zinc electrowinning cells. The TBP coextracts some ferric iron, cupric copper, lead and HCl with the zinc chloride. Laboratory

testwork indicates that the ferric iron can be removed in a second solvent extraction circuit. Traces of entrained organic are removed by absorption on activated carbon. If the zinc chloride solution requires further purification, lead and copper (and cadmium if present) can be removed by cementation on zinc dust; zinc oxide is used for pH adjustment. Chlorine produced by zinc chloride electrolysis is used to regenerated ferric chloride for the two-stage leach. The iron-removal SX reagent is stripped periodically with strong HCl and the strip liquor recycled to the stage 1 leach for acid make-up.

4.5 Zinc Chloride Electrowinning

Excellent quality zinc cathodes are produced by electrowinning from aqueous zinc chloride electrolyte. The quality of the zinc cathode is dependent on the purity of the zinc chloride feed solution. A current efficiency of 91% was achieved in a full-height (48") laboratory test-cell, using a current density of 323 Amps/m^2; the energy consumption is 3.5 kWh/kg of zinc at a cell voltage of 4.1 V.

4.6 Cadmium and Other Impurities

Cadmium recovery from the raffinate by adsorption on activated carbon is being studied; alternatively cementation on zinc dust is also possible.

Although some arsenic, antimony and bismuth are extracted from the concentrate during leaching they are effectively removed in the iron cementation step. Other impurities will build up in the recycled liquor; their control by a bleed stream taken from the raffinate is being evaluated in laboratory studies. The bleed stream treatment must yield environmentally acceptable solid and liquid waste streams. Oxyhydrolysis by turboaeration or high-temperature oxidation of the bleed stream is proposed as a means of removing the iron and recycling HCl and other metal values in

the circuit. Iron balance will likely determine the bleed volume requirements; present estimates are that a 5:1 recycle-to-bleed ratio will be required to maintain iron balance.

4.7 Raffinate Oxidation and Chlorination

Following cadmium recovery, the raffinate from zinc chloride solvent extraction is chlorinated for recycle to the second stage leach by direct contact with chlorine gas. Laboratory tests have shown that the oxidation of ferrous iron to ferric iron by chlorine gas is rapid and efficient; a packed column, in either co-current mode, or counter-current mode is effective.

5. Products of the FCL Process

The FCL process will yield the following products:

Zinc - special high grade quality cathode
Lead - corroding grade lead
Silver - cement cake containing 45% copper 34% iron and 1.2% silver can be produced (and upgraded if required)
Cadmium, (optimum recovery methods to be determined)
Sulphur, (optimum recovery methods to be determined)

6. Capital and Operating Costs

Table 6-1 and 6-2 show the capital and operating costs that have been estimated for the FCL process. The capital cost of $186 million is commensurate with that of the Sherritt Gordon pressure sulphuric acid (PSA) leach process ($199 million) applied to bulk concentrates. The operating costs are estimated at $55 million for a plant capacity of 100,000 tonnes per year of zinc or 55c per kg (24c/lb).

To get a perspective on the economic viability of the FCL process, its estimated profitability (i.e., netback to the mine)

is compared with that of two other processing alternatives, the Sherritt-Gordon PSA process and conventional processing. The comparison is shown in Table 6-3. The value recovered from the ore using the FCL process, of $150/tonne, is higher than the others because of the higher recoveries of zinc, lead and silver. The higher recoveries and the lower processing charges result in a netback to the mine of $81 per tonne of ore compared to $55-$57 per tonne for the other processes.

The use of the FCL process as an alternative to other available technologies, can provide advantages and flexibility in processing complex sulphide ores since it can efficiently treat lower grades of bulk concentrate. This could allow the concentrator circuit to be optimized for the production of higher grade selective concentrates while improving overall recovery of metal values in a bulk concentrate for processing in the FCL process.

Table 6-1

The FCL Process - Capital Cost Estimate - April 1987

(for a 100,000 tonne/y zinc plant)

	($000)	
Process Plant:		
Leach circuit	8,600	
Cementation $PbCl_2$ Crystallization	4,300	
Solvent extraction of $ZnCl_2$ and Iron Removal by SX	6,400	
Zinc Electrolysis	59,300	
Lead Electrolysis	10,000	
Other Process	11,100	
Process Buildings	17,000	
Auxilliary Plants	8,000	
Total Process		$124,700
Non-Process Plant:		
Utilities	10,800	
Tailings Disposal	5,000	
Other Capital	7,200	
Non-Process Buildings	4,200	
Indirects	3,700	
Engineering - Contracting	18,500	
Contingency	12,100	
Total Non-Process		$ 61,500
Total Capital		$186,200

Table 6-2

The FCL Process - Operating Cost Estimate - April 1987
(for a 100,000 tonne/y zinc plant)

	Annual Cost ($000)
Labour	$10,900
Hydrochloric Acid	5,000
Other Reagents	2,400
Other Supplies	4,400
Utilities	28,300
Other	4,100
Total Operating	$55,100

Table 6-3

The FCL Process - Profitability Comparison With Other Processes (per tonne of ore) - April, 1987

Item	Current Technology	CANMET FCL Process	Sherritt Pressure-H_2SO_4 Leach
Ore Value Recovered	$127	$150	$140
Capital Charges (10% - 15 y)	-	20	21
Processing Charges	-	49	62
Total Charges	72	69	83
Netback to Mine	$55	$81	$57